

SYNTHESIS OF STARCH-g-ACRYLAMIDE AND STARCH-g-METHYL METHACRYLATE

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ABSTRACT. Starch has been modified through graft copolymerisation with methyl methacrylate and acrylamide using ceric ammonium nitrate in nitric acid as initiator. The kinetic study of the copolymerisation reactions were investigated. The overall activation energies for these systems were determined.

INTRODUCTION

Graft copolymerisation of starch with vinyl monomers has been widely utilised to improve its blood compatibility, dialysis, thermal stability, elasticity, resistance to microbiological attack, sorbancy, ion exchange and mechanical properties (1-3). Starch and its derivatives are used as additives in paper, textile and pharmaceutical industries. The synthesis, properties and applications of graft and block copolymers of starch have been reviewed (1). Free radical, ionic, redox, condensation and ring opening polymerisation techniques have been utilised to graft copolymerise vinyl monomers onto starch. Pledger et. al. (2) and Egboh et. al. (3) have reported the graft modification of starch with acrylamide and methyl methacrylate respectively. Most of the reports dealing with the chemical modification of starch by grafting have concentrated on determining optimal grafting conditions.

There is a growing interest in the use of hydrophilic polymer membranes in biological and medical applications and in water pollution control. Polyacrylamide has been used as a dispersant/viscosity control agent during mud drilling, to control the loss of water from cement and as a flocculant during water purification. Shantora et. al. (4) found that modified poly (vinyl alcohol) membranes through grafting compared favourably with cellophane dialysis membranes in their permeability toward methanol and urea. Therefore, starch-g-acrylamide could be utilised in several applications.

As a part of a continuing programme in the modification of polymeric materials in our laboratory, this paper describes the graft copolymerisation reactions of methyl methacrylate and acrylamide onto starch using ceric ammonium nitrate as the initiator.

EXPERIMENTAL

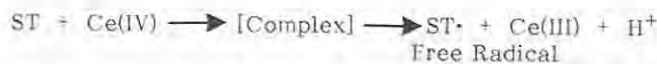
Chemicals. Soluble starch, ST, (BDH Chemicals) was dried in a vacuum oven. Methyl methacrylate, MMA, (BDH Chemicals) containing hydroquinone inhibitor was purified by washing with 5% sodium hydroxide and dried over anhydrous

calcium chloride. The dried monomer was fractionally distilled under reduced pressure. Acrylamide, AM, (BDH Chemicals) was purified by recrystallisation from chloroform. All solvents utilised were purified before use by standard techniques.

Synthesis and isolation of graft copolymers. The methods of synthesis and isolations of the starch-g-methyl methacrylates have been reported in our previous communication (3). The starch-g-acrylamide copolymers were prepared using similar techniques. The graft copolymers were isolated by selective solvent extraction with a soxhlet apparatus using water as solvent. The isolated copolymers were dried.

RESULTS AND DISCUSSION

Starch (ST) undergoes redox reaction with ceric ion to form polymer radicals capable of initiating graft copolymerisation of methyl methacrylate and acrylamide. The mechanism of copolymerisation reactions has been established (5). It involves the formation of starch-ceric complex which decomposes to polymeric starch free radical with the bond between carbons 2 and 3 broken, cerous ion and hydrogen ion. The generated starch radicals are responsible for the initiation of the graft copolymerisation reactions and the formation of the resulting homopolymers. The reaction schemes are represented below (1).



The graft yield was calculated using the expression:

$$\% \text{ Grafting} = \left(\frac{W_g - W_o}{W_o} \right) \times 100$$

where W_o and W_g represent the masses of original and grafted copolymers respectively. The determination of optimal grafting conditions for the synthesis of starch-g-methyl methacrylate has been reported (3). The effects of reaction conditions on the graft yields of starch-g-acrylamide have now been examined. Fig. 1 shows the variation of graft yield with reaction time. There is an increase in the graft yield at longer reaction time and reaches a maximum in about 4 h. The fall in graft yield could be due to the depletion in monomer and initiator concentration as well as the reduction in the available hydroxyl groups on the starch substrate. The graft yield increases at higher initiator concentration (Fig. 2) reaching a maximum at ceric ammonium nitrate concentration of 2×10^{-2} mol/dm³ and thereafter decreases. A high ceric ion concentration causes a decrease in the graft yield due to increased termination of starch radical and increased formation of homopolymer.

The effect of monomer concentration on the graft yield is shown in Fig. 3. There is a marked increase in the graft yield as the concentration of the acrylamide is increased, and this is due to increase in the molecular weight of the grafts. Under the conditions of the grafting experiments using ceric ion,

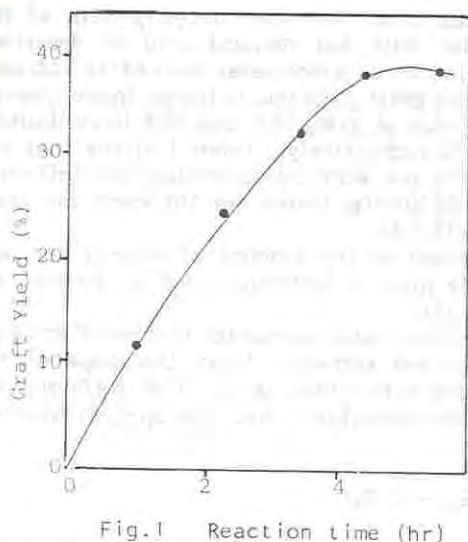


Fig. 1 Reaction time (hr)

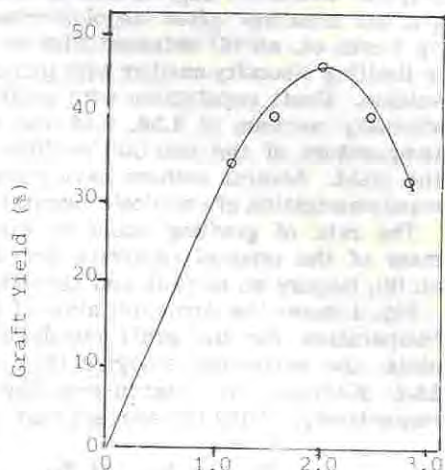

 Fig. 2 [initiator] x 10² mol.dm⁻³

Fig. 1. Variation of graft yield with reaction time. Starch = 0.5 g, [Ceric ion] = 1.66×10^{-2} mol/dm³, solvent = 40 cm³, [AM] = 0.25 mol/dm³, Temp = 55°C, HNO₃ = 0.1 M.

Fig. 2. Dependence of graft yield with Ceric ammonium nitrate initiator. Starch = 0.5 g, [AM] = 0.25 mol/dm³, Temp = 55°C, Solvent = 40cm³, Time = 4 h, HNO₃ = 0.1 M.

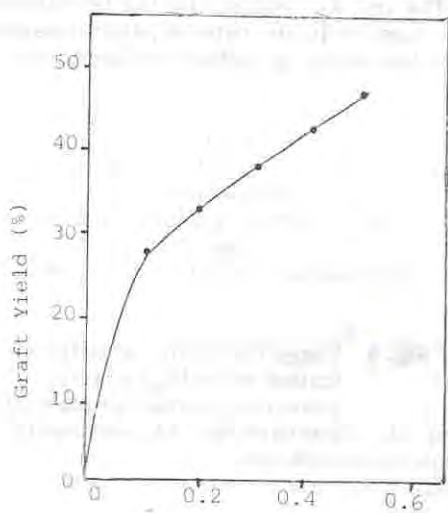
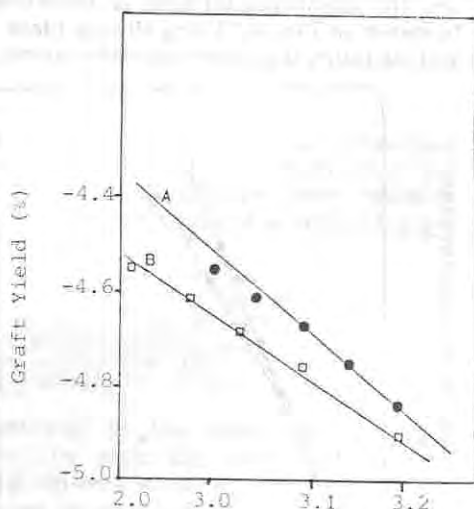

 Fig. 3 [Acrylamide] mol dm⁻³

 Fig. 4 $\frac{1}{T} \times 10^3$

Fig. 3. Effect of Monomer Concentration on the graft yield. Starch = 0.5 g, [Ceric ion] = 1.66×10^{-2} mol/dm³, Temp = 55°C, Solvent = 40 cm³, Time, 4 h, HNO₃ = 0.1 M.

Fig. 4. Arrhenius plots of grafting rates for the Starch-g-methyl methacrylate (A) and starch-g-acrylamide (B).

polymer backbone degradation is almost zero. Intrinsic viscosity data of the grafted branches after depolymerisation with hot mineral acid as described by Reyes et. al. (6) obtained with an Ubbelohde viscometer showed an increase in limiting viscosity number with increased graft yield due to higher hydrodynamic volume. Graft copolymers with graft yields of 27%, 35% and 45% have limiting viscosity numbers of 0.59, 0.68 and 0.72 respectively. Table 1 shows that the temperature of the reaction medium and the acid concentration also influence the yield. Several authors have reported similar trends for the ceric ion graft copolymerisation of cellulosic substrates (2,7,8).

The rate of grafting could be expressed as the amount of add-on per unit mass of the original substrate per unit time, a technique used by Kaleem et. al. (9), Hegazy et. al. (10), and Egboh (3, 11).

Fig. 4 shows the Arrhenius plots of grafting rates versus the inverse of absolute temperature for the graft copolymerisation systems. From the slope of the plots, the activation energies (E_a) were determined to be 33.6 KJ/mole and 23.2 KJ/mole for starch-g-methyl methacrylate and starch-g-acrylamide respectively. Using the concept that

$$E_a = \frac{1}{2} E_d + \frac{1}{2} E_{tr} + (E_p - \frac{1}{2} E_t)$$

where E_d is the activation energy of initiator decomposition, E_{tr} is the chain transfer process's activation energy, E_p is activation energy of propagation process and E_t is the termination process's activation energy. Hence utilising the value of $(E_p - \frac{1}{2} E_t) = 18.9$ KJ/mole for methyl methacrylate (12), the $\frac{1}{2}(E_d + E_{tr})$ for the ceric ammonium nitrate initiator with regard to the starch-g-methyl methacrylate system was evaluated to be 14.7 KJ/mole.

The logarithmic plots of grafting rates against the logarithm of monomer and ceric ammonium nitrate concentrations gave straight lines whose slopes are the exponents (orders) of reactions. The $\log R_p$ against the $\log [\text{monomer}]$ is shown in Fig. 5. Using similar plots with respect to the rate of polymerisation and initiator, the order was determined. For the starch-g-methyl methacrylate,

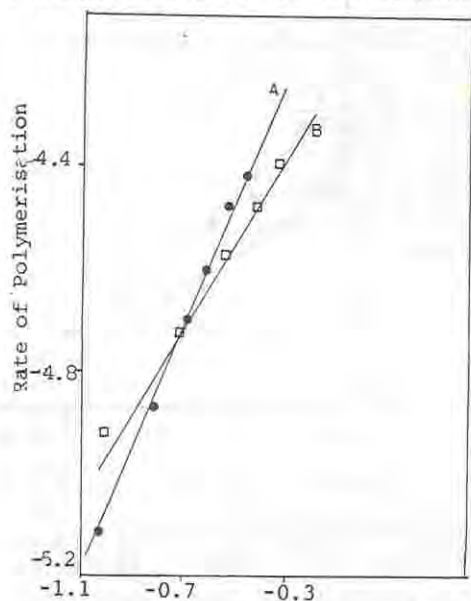


Fig. 5. Logarithmic plot of polymerisation rates (R_p) against monomer concentration; methyl methacrylate (A) and acrylamide (B).

Fig. 5 $\log [M]$

Table 1. Effect of temperature and acid concentration on graft yield.

Temperature (°C)	Acid molarity (M)	Graft yield (%)
30	0.1	27.0
40	0.1	31.4
50	0.1	35.6
60	0.1	40.2
70	0.1	46.2
55	0.1	37.8
55	0.2	40.9
55	0.3	47.5
55	0.4	34.0
55	0.5	28.1

Starch = 0.5 g, Time = 4 h, Solvent = 40 cm³
 [Ceric ion] = 1.66 x 10⁻² mol/dm³, [AM] = 0.25 mol/dm³.

$$R_p = K_1[MMA]^{1.2}[Ce(IV)]^{0.82}$$

at lower initiator concentration and

$$R_p = K_1'[MMA]^{1.2}[Ce(IV)]^{0.47}$$

at higher initiator concentration.

Furthermore, for the starch-g-acrylamide system

$$R_p = K_2[AM]^{0.81}[Ce(IV)]^{0.73} \text{ and}$$

$$R_p = K_2'[AM]^{0.81}[Ce(IV)]^{1.12}$$

at lower and higher initiator concentrations respectively.

The differences in the rate equations at low and high initiator concentrations could be due to the nature of the termination processes. At lower ceric ion concentration, termination seems to proceed mainly through chain transfer and radical coupling while at higher concentration, termination is predominantly controlled by ceric ion.

Ogiwara et. al. (5) have shown that

$$R_p = \frac{K_p}{K_t} [M]^2 \left\{ K_1 + \frac{K_1 K_d K [Cell - H]}{K_o [Ce(IV)]} \right\}$$

and hence, the grafting rate is proportional to the square of monomer concentration and inversely proportional to the ceric ion concentration. Our results do not agree with those postulated by Ogiwara et. al. (5). The reversibility of the reaction steps in the initiation process as proposed by Varma et. al. (13) and other yet unknown reaction steps may account for our observations. Several authors have observed grafting rates to be proportional to monomer concentration (14,15). The differences in the order of graft copolymerisation reactions between the starch-g-methyl methacrylate and the starch-g-acrylamide systems could be due to differences in their reactivity during copolymerisation as well as due to solvent effects.

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